

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE PROGRAM/PROJECT STATUS REPORT

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1. Program/Project Identification No. DE-FC26-98FT40320	2. Program/Project Title Subtask 2.2 – Fine Particulate Characterization and Source Apportionment	3. Reporting Period 4-1-02 through 6-30-02
4. Name and Address Energy & Environmental Research Center University of North Dakota PO Box 9018, Grand Forks, ND 58202-9018		5. Program/Project Start Date 4-15-98
		6. Completion Date 3-31-03

7. Approach Changes

☒ None

8. Performance Variances, Accomplishments, or Problems

Activity 1 – Fractionation of Organics from Air Particulates with Subcritical Water

Introduction

The toxic effects on health of fine particulate aerosol (particles smaller than 2.5 µm) are discussed in a number of studies.^{1,2} In contrast to inorganic aerosols, which are often well characterized, only ca. 15%–50% of the organic carbonaceous (OC) particulate mass has been characterized. The characterized compounds are almost exclusively nonpolar.³ The limited knowledge on OC fractions is due to the use of organic solvents which are able to extract only nonpolar or slightly polar organics. In addition, polar compounds cannot normally be analyzed via GC–MS (gas chromatography–mass spectrometry). Consequently, the toxicity of organic aerosols has been primarily studied for nonpolar OC (for example, polycyclic aromatic hydrocarbons [PAHs]), while the toxicity of significant polar fractions of OC is not known. Moreover, with conventional solvent extracts, toxicity tests on OC are difficult to perform because the solvents employed are toxic for biological systems. Finally, polar organics may also be important for mobilizing toxic metals from air particulates in biological systems by chelation reactions.⁴

☐ None

Continued . . .

9. Open Items

☒ None

10. Status Assessment and Forecast
Please see attached.

☐ No Deviation from Plan is Expected

11. Description of Attachments

8. Performance Variances, Accomplishments, or Problems (continued)
10. Status Assessment and Forecast

☐ None

12. Signature of Recipient and Date

13. Signature of U.S. Department of Energy (DOE) Reviewing Representative and Date

SUBTASK 2.2 – FINE PARTICULATE CHARACTERIZATION AND SOURCE APPORTIONMENT

Quarterly Status Report

April 1 – June 30, 2002

8. Performance Variances, Accomplishments, or Problems (continued)

Subcritical water has not previously been used to fractionate OC from air particulates, but should have the ability to extract a broad range of polar to low-polarity OC, as well as to provide extracts in a solvent (water) which is directly useful for biological tests. At lower temperatures (e.g., 50° to 100°C), water can extract polar compounds. With higher temperatures (e.g., to 250°C), the polarity of water decreases, and therefore, nonpolar compounds can be extracted.⁵ Earlier studies have shown that compounds of different polarities, such as phenols, PAHs (polycyclic aromatic hydrocarbons), and alkanes, can be sequentially extracted from a petroleum waste sludge by increases in subcritical water temperature.⁶ The use of water also has the advantage that extracts are suitable for toxicological studies.

Results and Discussion

During this quarter, the following tasks were completed.

Elemental Analysis

Additional characterization of wood smoke and diesel exhaust particulate subcritical water fractions (25°–300°C) was performed. Verification of previous gravimetric determinations showed that the initial data were not correct, because of unexpected changes in the weights of Teflon-lined caps. Figure 1 shows new data including corrected CHN and sulfur contents. The gravimetric data show the most polar water (25°C) extracted the highest mass of particulate. The total extracted particulate with subcritical water extraction (25°–300°C) was 42 wt% and 34 wt% for wood smoke particulate and diesel exhaust particulate, respectively. Figure 1 shows that C,H,N, and S composition corresponds to approximately 40–60 wt% of the extracted mass for each fraction. In order to determine if the carbon extracted with water is mainly organic carbon (as opposed to carbonate or graphitic carbon), elemental carbon (total carbon) values were compared to total organic carbon (TOC) values in the water extracts (Figure 2). Good agreement between elemental carbon and TOC values demonstrates extracted carbon is essentially all organic. Organic carbon determinations can be used to approximate the extracted mass of organic compounds including oxygenated organics by multiplying the TOC values by a factor estimated to include “average” oxygen content. The most common factor is 1.4, which corresponds mainly to aerosols in urban areas.⁷ Recently, it has been shown that for aerosols heavily impacted by wood smoke, a factor of 2.2–2.6 is more suitable.⁷ Therefore for an estimation of total organics in wood smoke and diesel exhaust particulate, which includes oxygenates, we have used average factor of 2.4 and 1.4, respectively. For most of the wood smoke particulate water fractions, the estimated total organic compound mass corresponds to (or exceeds) the amount extracted. For diesel exhaust, the estimated total organic compound mass is lower than total extracted, probably due to the presence of inorganic compounds, especially in the most polar (25°C) fraction.

The Toxicity Test – Polytox Was Completed

In a previous report, the importance of individual fractions was evaluated with three different toxicity tests: Polytox based on bacterial respiration, SOS chromotest based on DNA damage, and cytotoxicity based on the viability of mammalian cells. Each test was performed on concentrated water fractions and on separate water fractions that had been dried and then dissolved in dimethyl sulfoxide (DMSO) (because the cooled concentrated water extracts precipitated). To complete the toxicity studies, the results from Polytox on water fractions, which were dried and dissolved in DMSO, were obtained. The diesel exhaust particulate water fraction obtained at 25°C (polar materials), which was dried and dissolved in DMSO, exhibited the highest toxicity (60% inhibition). Previously, 25°C fractions dissolved in water also showed significant inhibition of bacterial respiration. The nonpolar fractions obtained at 250° and 300°C also had shown 15% inhibition of bacterial respiration. The wood smoke particulate water fractions of 25° and 50°C (dried and dissolved in DMSO) inhibited bacterial respiration (18% and 10%, respectively), and increased toxicity of 15% was also observed for the fraction extracted at 200°C.

The Genotoxicity Test-SOS Chromotest with Metabolic Activation Was Completed

The previous genotoxicity tests studied the toxicity of samples directly. Because a number of compounds (promutagens) exhibit genotoxicity after they are metabolically activated, additional tests with metabolic activation (using rat liver microsome induced by Aroclor S9) were performed. While no genotoxic response of wood particulate fractions was observed directly, the genotoxicity after metabolic activation was found in fractions from 50°, 250° and 300°C water extractions. The genotoxicity of the least polar fractions can be explained by increased concentrations of PAHs. The genotoxicity test with and without activation of diesel exhaust particulate showed increased genotoxicity of both the 150° and 200°C fractions, which may correspond to increased concentration of nitroaromatics.

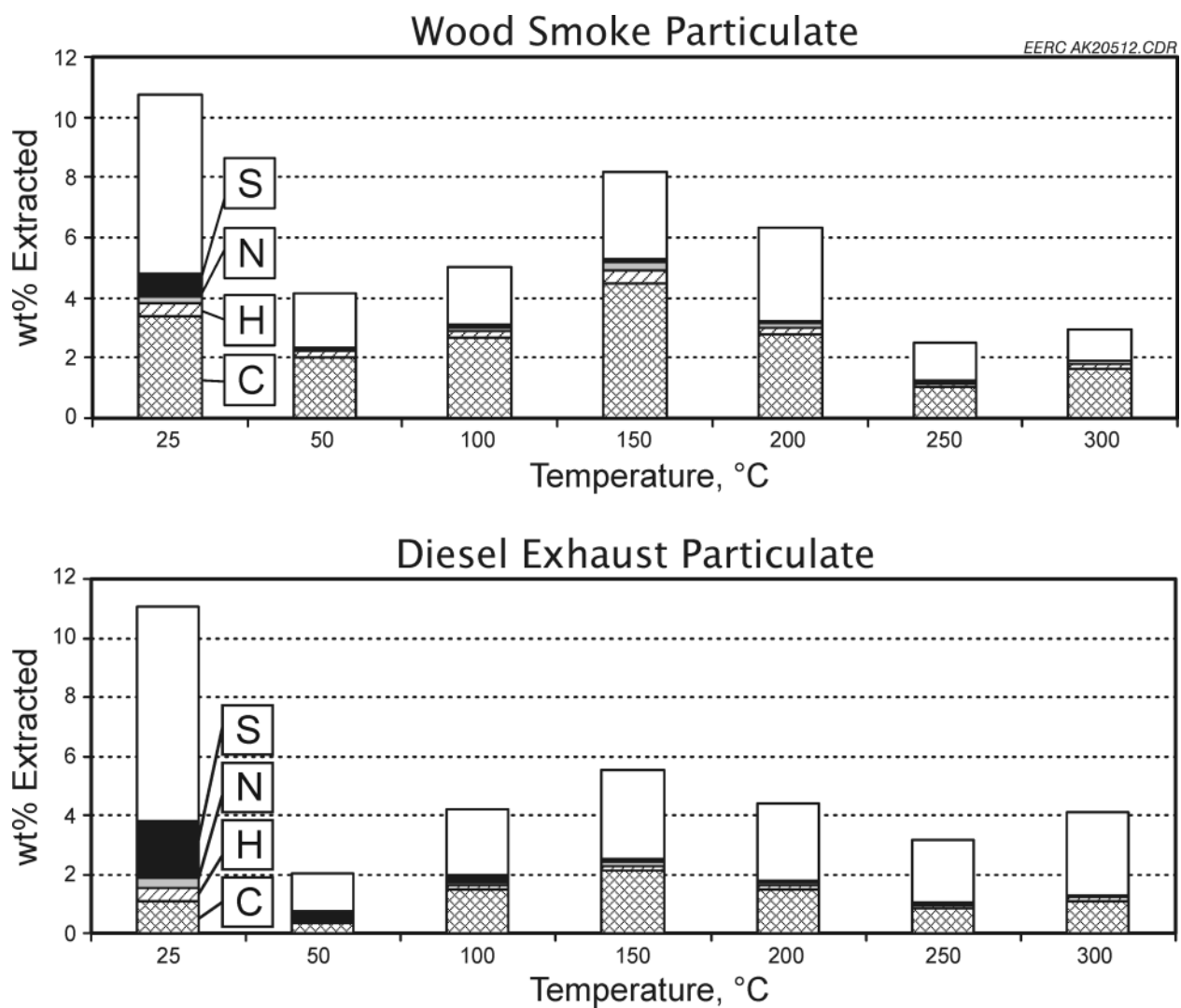


Figure 1. CHN and sulfur determination on diesel exhaust and wood smoke particulate fractions extracted sequentially with subcritical water at temperatures of 25°–300°C.

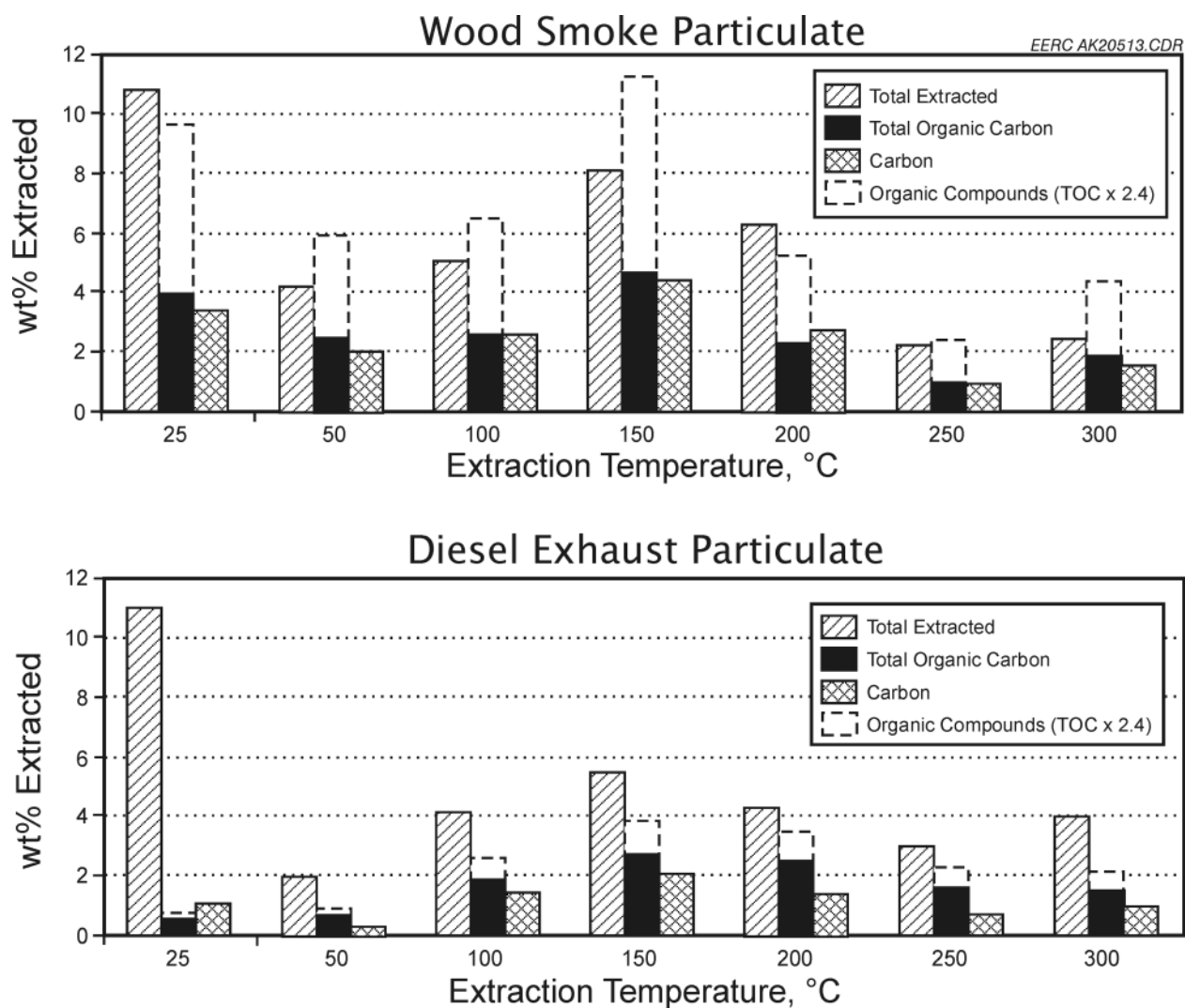


Figure 2. Determination of extracted mass, total organic carbon, carbon, and estimates of organic compound mass of wood smoke and diesel exhaust particulate fractions extracted sequentially with subcritical water at temperatures 25°–300°C.

Activity 2 – Fine Particulate Characterization and Source Apportionment

Ambient particulate matter (PM) sampling and automated scanning electron microscopy (ASEM) are being used to characterize and evaluate the sources of PM ≤ 2.5 μm (in aerodynamic diameter [$\text{PM}_{2.5}$]) at three rural sites. Land use in the sampling site locations is dominated by ranching and small-grain farming. Potential sources of PM in these areas include diesel- and gasoline-fueled motor vehicles, fugitive dust from gravel roads and agriculture, vegetation, fires, an oil refinery, and coal-fired power plants. Site 1 is remote from large population centers and industrial activity; however, several large (500-MWe) coal-fired power plants and a large coal gasification facility are within 110–150 km of the site. Sampling was performed in late summer during a period of small-grain harvesting. Land use near Site 2 is dominated by ranching. A well-traveled paved and an infrequently traveled gravel road exist within approximately 60 m of the sampling site. Sampling at this site was performed concurrent with haying activities. An oil refinery and several coal-fired power plants are located approximately 95 km west of Site 2. Site 3 is remote from large population centers, industrial activity, and thermal power plants. Sampling was performed during a period of spring tillage and planting.

$\text{PM}_{2.5}$ samples were collected using an automatic cartridge collection unit attached to a tapered element oscillating microbalance (TEOM Model 1400a) for ASEM analysis. An ASEM method has been developed to size and chemically classify individual particles composing $\text{PM}_{2.5}$. The particle chemical compositions (C, N, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, and Fe) were classified into chemical and mineral groups. Eight major chemical categories were identified and used to classify $\text{PM}_{2.5}$. These are quartz, feldspar, clays (e.g., kaolinite, chlorite, muscovite, biotite, and illite), Na–K salts (i.e., NaCl and KCl), carbonates (i.e., calcite, dolomite, ankerite, siderite), iron-rich (e.g., pyrite, magnetite, ilmenite, and hematite), sulfur-rich (e.g., anhydrite and gypsum), and unclassified, which generally consists of chemically complex particles such as mixed clays, clay-coated mineral grains, and/or organic compounds. As illustrated in Figures 1–3, 79% to 87% of the $\text{PM}_{2.5}$ consists of unclassified and organic components. The particles in these classification categories are mostly spores, pollen, soil, and fugitive dust. The remaining 13% to 21% of $\text{PM}_{2.5}$ collected at the sites is inorganic rich. The clays, quartz, carbonates, and feldspars are primarily associated with fugitive dust from nearby gravel roads and fields. The alkali salt contents of all three samples are very consistent, suggesting a regional and perhaps natural source for this particle type. $\text{PM}_{2.5}$ samples from Sites 1 and 3 are compositionally similar. $\text{PM}_{2.5}$ from Site 2, however, contains a greater proportion of sulfur-rich particles, presumably composed of secondary sulfate compounds.

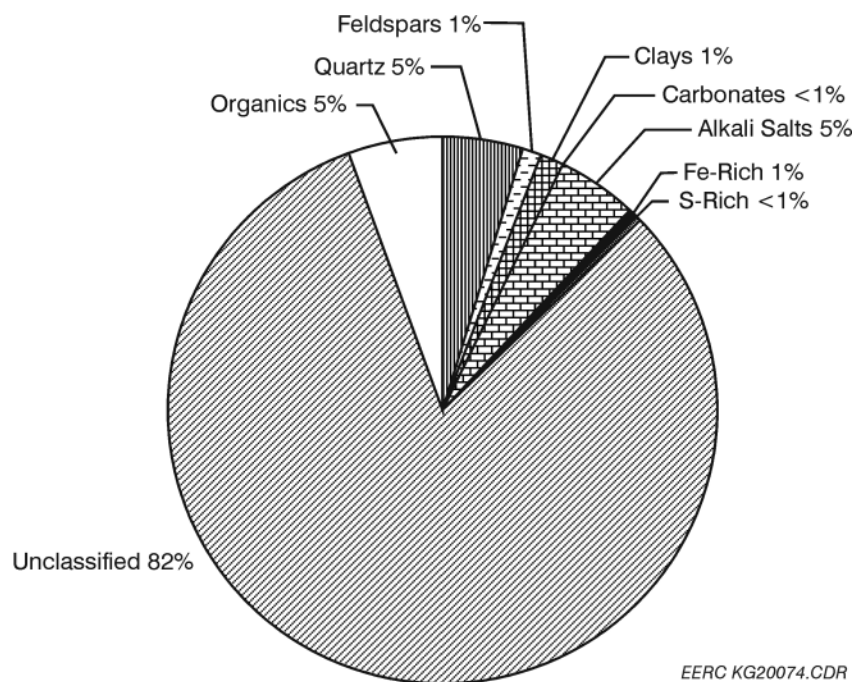


Figure 1. Chemical classification of PM_{2.5} from Site 1.

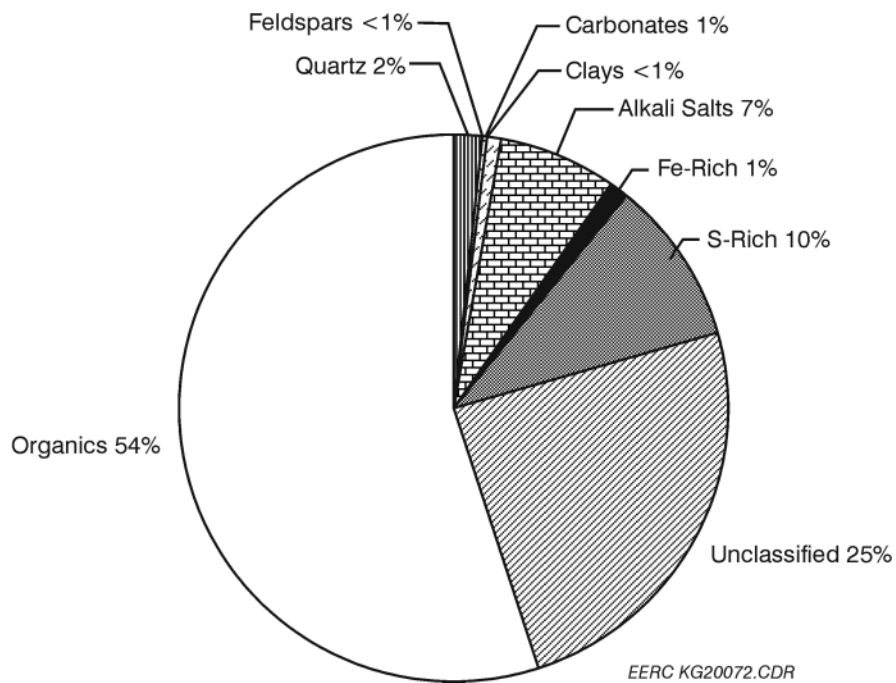


Figure 2. Chemical classification of PM_{2.5} from Site 2.

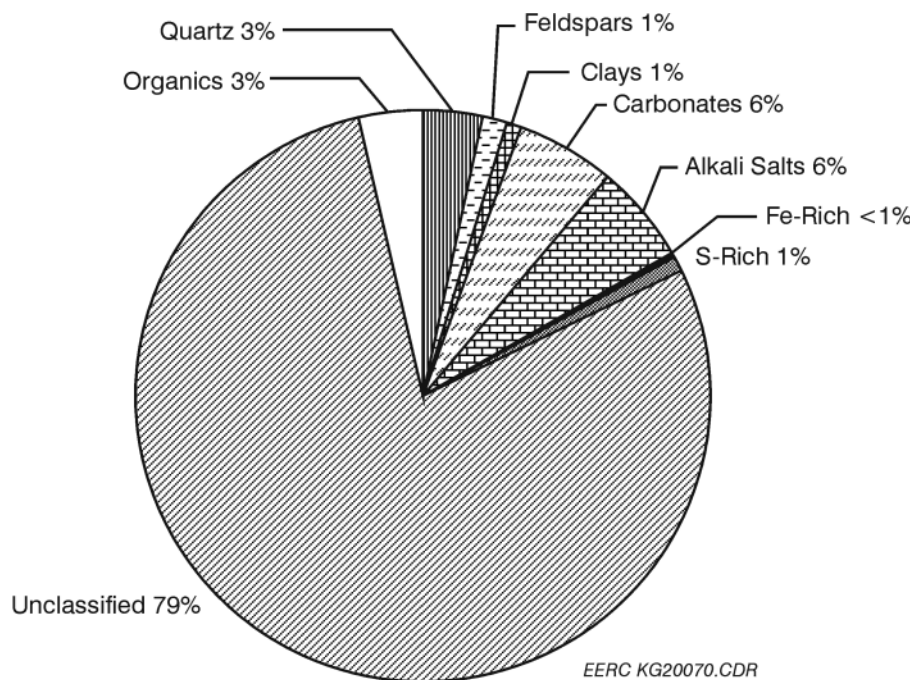


Figure 3. Chemical classification of PM_{2.5} from Site 3.

Activity 3 – Characterization of Indoor Air Quality

During this quarter, we have had extensive discussions with agencies including the National Candle Association, American Lung Association, and various candle manufactures for possible cooperation. According to the discussions, even though the candle industries are very conservative and would not release information on their candles to the public, the American Lung Association shows a strong interest in further discussion on candle issues.

10. Status Assessment and Forecast

Activity 1 – Fractionation of Organics from Air Particulates with Subcritical Water

The following tasks will be performed:

- The suitability of toxicity tests: SOS chromotest and cytotoxicity test will be evaluated for pesticides.
- Initial tests on subcritical water extraction of ambient aerosol sample obtained from Prof. Allen L. Robinson from Carnegie Mellon University, Pittsburgh, PA.

Activity 2 – Fine Particulate Characterization and Source Apportionment

The following tasks will be performed:

- Present paper at ACS meeting in Boston.
- Conduct PM sampling at urban sites.

Activity 3 – Characterization of Indoor Air Quality

A test chamber for burning candles is in the design process. The test chamber will have the capabilities for controls of the airflow pattern inside the chamber and have the access to emission sampling from burning candles. The test chamber will be ready for candle tests next quarter.

References

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